The Effect of Molecular Structure on Liquid Crystal Properties in Binary Mixtures

Jianwei Wu, Hiroaki Okamoto,* and Shunsuke Takenaka
Department of Materials Science and Engineering, Faculty of Engineering,Yamaguchi University,
2557 Tokiwadai, Ube, Yamaguchi 755-8611

(Received January 18, 2001; CL-010052)

The mesomorphic properties of some binary mixtures consisting of 4-alkoxyphenyl 4-(2-R- or 4-R-3-alkoxybenzoyloxy)benzoates (R=H, CH_3, Br, or CN) and 4-cyano-4'-octyloxybiphenyl or 4-pentyloxyphenyl 4-[(4-octyloxy)benzoyloxy]benzoate were examined. In the binary phase diagrams an enhanced and/or induced smectic A phases were observed, even if both components have terminal polar group. The mesomorphic properties are discussed in terms of both electrostatic nature of substituents and molecular shapes of both components.

It has been known that in a lot of binary mixtures consisting of “polar” and “non-polar” liquid crystals (LCs) a smectic A (Sm A)-nematic (N) or a Sm A-isotropic (I) transition temperature shows a notable enhancement or an induction of the Sm A1 phase around the center of the diagram.[1,2] In such mixtures, usually, polar interactions such as electron donor–acceptor (EDA)[3] or dipole–dipole (induced) interaction[4] have been supposed to be responsible for the phenomena. Recently, a relative importance of molecular shapes of both compoments has been supposed.[5] As far as we know, however, the electro-static effect on the thermal properties of the enhanced or the induced Sm A phase has not been clarified.

In our earlier paper, we described that a molecular shape involving conformational isomerism around the alkoxy group is an important factor in determining the LC properties.[6] In LC molecules having a lateral alkoxy group, for example, the following conformational isomers distribute in the LC states as shown in Figure 1. Compounds having a methyl group at the R_2 position exhibit the most stable N phase due to preferential formation of Conformer A. Compounds having a methyl group at the R_1 position also exhibit the N phase in spite of the bent conformation (B). On the other hand, the unsubstituted compounds (R_1=R_2=H) are non-mesogenic, probably due to the co-existance of both conformers. A distinctive characteristic for the 3-alkoxy compounds is that their molecular structures can be easily modified by substitution at the 2 or the 4 position.

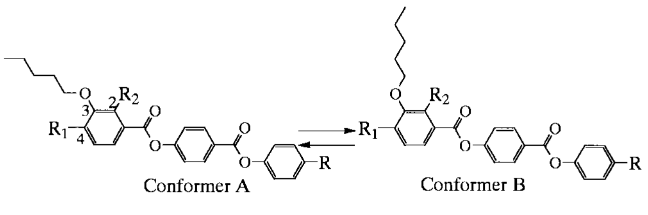
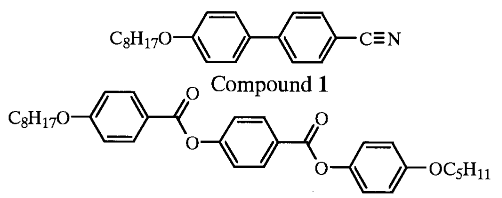
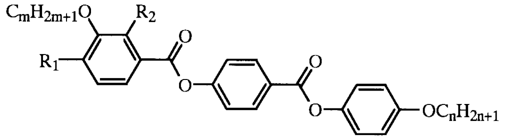


Figure 1. Conformational isomerism of 3-alkoxybenzoate compounds.

In this paper, we want to show the substituent effect on the smectic properties in binary mixtures. For this purpose, we prepared some related compounds, as shown in Figure 2.



Compound	Transition temperatures (T/°C)
2[7]	C•93•Sm C•136•Sm A•156•N•200•I



	Compounds	Transition temperatures (T/°C)
3[6]	R_1, R_2 = H, m=5, n=8	C•88[•N•43]•I
4[6]	R_1 = H, R_2 = CH_3, m=6, n=8	C•77•N•83•I
5[6]	R_1 = CH_3, R_2 = H, m=6, n=8	C•82(•Sm C•44•N•67)•I
6[8]	R_1 = Br, R_2 = H, m=5, n=6	C•78•Sm C•90•Sm A•91•N•92•I
7[9]	R_1 = CN, R_2 = H, m=5, n=8	C•92•Sm C•116•N•120•I

Figure 2. Molecular structures and phase transition temperatures of compounds **1**–**7**. Parentheses and brackets indicate monotropic and virtual transition temperatures, respectively. Sm C indicates a smectic C phase.

Compound **3** is a conformational mixture of A and B, and the entire molecular shape is fairly dependent on the physical circumstances. Compound **4** is supposed to keep a good linearity of the entire molecular shape, due to repulsive interaction between the alkoxy and the adjacent methyl groups. Compounds **5**, **6**, and **7**, on the other hand, are intrinsically bent molecules, due to a repulsive interaction between the alkoxy group and the adjacent substistuent. In this work, 4-cyano-4'-octyloxybiphenyl (**1**) and 4-pentyloxyphenyl 4-[(4-octyloxy)benzoyloxy]benzoate (**2**) were used as a reference compound for the binary mixtures. Although 4-alkoxy-4'-cyanobiphenyl is a linear molecule when alkoxy group is short, compound **1** is not linear but bent molecule, due to the bond angle of C–O–Ph (116°). Compound **2** is also supposed to be a similar conformational mixture to **3** due to two terminal alkoxy groups.

The binary phase diagrams for the mixtures of **1**/**3** and **3**/**7** are shown in Figure 3. It would be reasonable to assume that in the diagrams the mesomorphic properties of both sides are mainly dependent on those of each compoment, and those around the center are affected by both components. For the mixture of **1**/**3** in Figure 3(a), the diagram shows a notable enhancement of the Sm A-N (I) transition temperature around the center of the diagram. For the mixture of **3**/**7** in Figure 3(b), on the other hand, an induced Sm A phase is observed around the center of the diagram. These results indicate that both compoments form a 1:1 complex of each component in the Sm A phase, giving rise to the enhancement of the Sm A-I transition temperature.

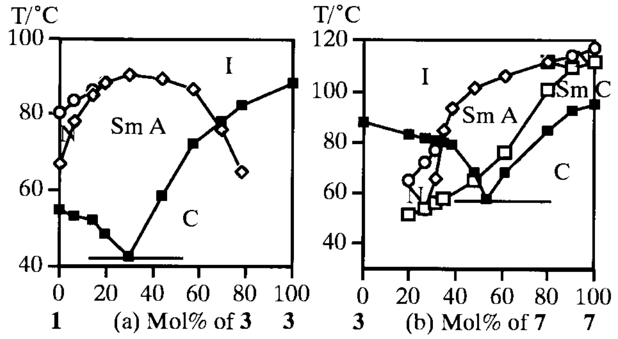


Figure 3. Binary phase diagrams for the mixtures of (a); **1**/**3** and (b); **3**/**7** . ○; N-I, ◇;Sm A-N (I), □; Sm C-Sm A (N), and ■; C-Sm A, Sm C, or I transitions.

A similar phase behavior was recognized in the other binary mixtures, so that only the Sm A-N (I) transition temperatures are plotted against the molar concentrations in Figure 4. In Figure 4(a), all of the Sm A-N (I) transition temperature show the enhancement around the center of the diagrams. One of the notable facts is that the maximal Sm A-N (I) transition temperatures for the mixtures of **1**/**3** and **1**/**4** are lower than those for the other mixtures. The other is that, interestingly, the Sm A-I transition temperature for the mixture of **1**/**7** also shows the enhancement, while both components have a terminal cyano group, and the maximal Sm A-I transition temperature is similar to those for the mixtures of **1**/**5** and **1**/**6**.

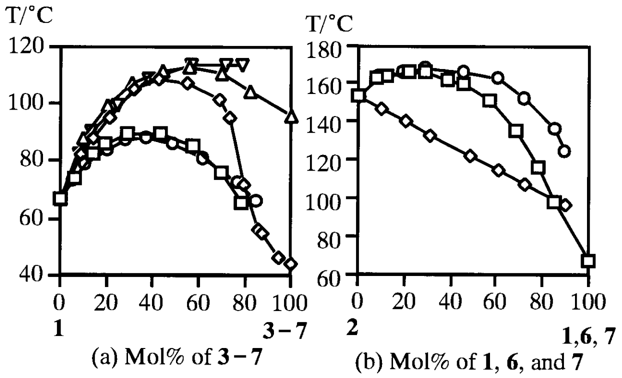


Figure 4. Plots of Sm A-N (I) transition temperatures vs mol% of components for the mixtures of (a); **1**/**3** (□), **1**/**4**(○), **1**/**5** (◇), **1**/**6** (△), and **1**/**7** (▽), and (b); **2**/**1** (□), **2**/**6** (◇), and **2**/**7** (○).

Furthermore, a similar enhancement of the Sm A-N transition temperature was observed in the binary mixtures of **4**–**6**/**7**. In Figure 4(b) the Sm A-N (I) transition temperatures for the mixtures of **2**/**1** and **2**/**7** corresponding the usual "polar–non-polar" binary system[2] show the enhancement of the Sm A-N (I) transition temperature. The Sm A-N transition temperature for the mixture of **2**/**6** corresponding to the usual "non-polar–non-polar" binary system shows a linear correlation against the molar concentration of the components. The Sm A-N transition temperatures for the mixtures of **2**/**3**–**5** also show the linear correlation.

From these results, the molecular properties of the components are correlated with the smectic properties, as shown in Table 1.

Table 1. The effect of molecular structures on smectic properties in binary mixtures

	Comp. 1	Comp. 2	Comp. 3, 5–7	
	3-H 4-CN	3-H 4-OR	3-OR 4-CN	3-OR 4-H, CH_3, Br
Comp. 1 (4-CN)		Enhanced	Enhanced	Enhanced
Comp. 2 (4-OR)			Enhanced	Linear
Comp. 7 (4-CN)				Enhanced

The following facts are noteworthy in connection with the enhancement or the induction of the Sm A phase in binary mixtures. First, the abnormal behavior of the Sm A phase occurs not only in so-called "polar–non-polar" LC systems but also in "polar–polar" ones. However, one of the components must be a "polar" LC, like **1** and **7**. Second, the maximal Sm A-N (I) transition temperature is almost independent of the electrostatic nature of the terminal substituent at the R_1 position of compounds **5**–**7** (see curves **1**/**5**, **1**/**6**, and **1**/**7** in Figure 4(a)). That is, the effective order for the Sm A-N (I) transition temperature is CH_3–Br–CN. Third, the long alkoxy group at the terminal position (the 3 or the 4 position in **2**–**7**) is necessary in order to show the abnormal behavior, similar to usual binary mixtures.[2] Thereby, the conformation of the alkoxy group at the 3 position also affects the the maximal Sm A-N (I) transition temperature.

Further examination is now underway.

References and Notes

1 J. W. Park, C. S. Bak, and M. M. Labes, *J. Am. Chem. Soc.*, **97**, 4398 (1975).
2 H. Kelker and R. Hatz, "Handboook of Liquid Crystals," ed. by C. Schumann, Verlag Chemie (1980).
3 D. Demus, A. Hauser, G. Pelzl, V. Bottger, and S. Schonburg, *Cryst. Res. Technol.*, **20**, 381 (1985).
4 M. Marcos, E. Melenoez, M. B. Ros, and J. L. Serrano, *Mol. Cryst. Liq. Cryst.*, **167**, 239 (1989).
5 G. R. Saad and R. I. Nessim, *Liq. Cryst.*, **26**, 629 (1999).
6 J. Wu, H. Okamoto, and S. Takenaka, *Chem. Lett.*, **2001**, 116.
7 T. Tasaka, H. Okamoto, V. F. Petrov, and S. Takenaka, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A*, **357**, 67 (2001).
8 Unpublished results in our laboratory.
9 H. Okamoto, A. Umeda, and S. Takenaka, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A*, **317**, 111 (1998).